

EPOXY NANOCOMPOSITE ADHESIVES

A. Pegoretti*, A. Dorigato

*Department of Materials Engineering and Industrial Technologies, University of Trento, via Mesiano
77, 38123 Trento, Italy*

**alessandro.pegoretti@unitn.it*

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Abstract

Epoxy resins are excellent adhesives widely employed to join metals, ceramics, plastics and composites to themselves and to each other. The introduction of inorganic nanoparticles to polymeric adhesives at low percentages may lead to substantial improvements of their mechanical performances in structural joints. Recently, this research group succeeded in enhancing the performances of epoxy adhesives by adding proper amounts of zirconia nanoparticles, alumina nanoparticles, and layered silicates. The main benefits were quantified as an increase of the glass transition temperature, tensile elastic and ultimate properties, and fracture toughness of bulk adhesives. Moreover, a marked improvement of both static and fatigue resistance in metal and composite bonded joints was obtained.

1 Introduction

The use of adhesives in place of traditional fasteners is becoming increasingly popular in structural design, because of their reduced weight and cost. In fact, high-performance adhesives are needed for joining metals, composites, ceramics and plastics to themselves and to each other. They are utilized in a variety of applications in aerospace, automotive, electronic, domestic household, oil and other industries. A comprehensive review of the advances in bonding with structural adhesives has been recently edited by Dillard [1].

From a general point of view, epoxy resins display excellent properties as adhesives [2]. Nevertheless, they are inherently brittle materials and several investigations were thus performed to increase the fracture toughness of these systems. In particular, it was reported that the crack resistance of structural epoxy adhesives could be improved by the incorporation of elastomeric micro- or nano-domains [2-5]. As an example, He et al. [6] analyzed the fracture behavior of rubber modified epoxy systems, showing that the toughness increased up to an optimal rubber content. On the other hand, the addition of rubber to a glassy epoxy network is often detrimental for the rigidity and long-term (creep) mechanical properties of the adhesive [7]. Another possibility that recently emerged to increase the fracture toughness of epoxy adhesives is the incorporation of rigid nanofillers [8, 9]. Moreover it was recently proven that the addition of small quantities of inorganic nanoparticles in polymeric adhesives can improve the shear resistance of structural joints [10]. The enhancement of the mechanical performances of the epoxy adhesives can be directly related to the improved shear strength of joints bonded with the nanomodified adhesive [11].

In some recent studies, we focused our attention on the possibility to increase the mechanical performances of both metal and composite bonded joints by the addition of various types and

amount of nanofillers to an epoxy resin. In particular, the effects of zirconia nanoparticles [12], alumina nanoparticles [13] and organo-modified layered silicates [14] on the thermo-mechanical properties and the bonding efficacy of an epoxy adhesive have been investigated. In this manuscript, the most relevant results will be presented, compared and critically discussed.

2 Materials and testing methods

2.1 Materials

A two-component epoxy resin commonly utilized for the preparation of structural adhesives was supplied by Elantas Camattini (Collecchio, Italy). In particular, EC57 epoxy base (density and viscosity at 25 °C of 1.15 g cm⁻³ and 1,500 mPa s, respectively) and W635 amine hardener (density and viscosity at 25 °C of 0.95 g cm⁻³ and 750 mPa s, respectively) were mixed at a weight ratio of 100/50.

Synthesis of zirconia nanoparticles was conducted in hydrothermal conditions starting from a 0.1 M solution of tetra-n-propylzirconate (TPZ, Aldrich) using a commercial microwave-heated flow vertical tube reactor (MLS ETHOS CFR Continuous Flow Reactor) in agreement with a procedure described elsewhere [15]. TPZ, caproic acid (CA, Aldrich) and ethanol (EtOH, Eurobase) were used as received without further purification. Synthesis of zirconia particles was performed by slow addition of an alcoholic solution containing CA (0.016 M) and TPZ (0.1 M), previously reacted for 30 min at room temperature, to a mixture of EtOH and water (50:1 molar ratio) directly to the inlet of the reactor. The flow rate was fixed at 50 ml/min as optimized to obtain spherical monomodal nanoparticles. The water concentration was fixed to 0.6 M. After the synthesis reaction, the powder was filtered, washed, dried and calcined at 600 °C for 4 h in order to improve its crystallinity.

Fumed alumina nanoparticles, commercially available under the trade name of Aeroxide AluC, were supplied by Degussa (Dusseldorf, Germany). According to the producer's data, these nanofillers are characterized by a mean primary nanoparticles diameter of 13 nm and a specific surface area of 100 m²/g. Alumina nanoparticles were utilized as received and after a calcination process, conducted at 600 °C for 4 h in an air oven.

Two different organo-modified layered silicates (Cloisite 30B and Cloisite 25A), provided by Southern Clay Products, Inc. (Gonzales, Texas) were used. In a previous investigation of this research group [16] water-clay equilibrium contact angle measurements were successfully adopted to rank several organo-modified layered silicates accordingly to their hydrophobicity. In particular, it was proven that Cloisite 25A was more hydrophobic than Cloisite 30B.

2.2 Preparation and characterization of bulk adhesives

Various filler contents (from 0.5 to 5 wt%) were added to the epoxy adhesive according to dispersion procedures carefully described in [12-14]. In general, the fillers were added to the epoxy base, mechanically mixed in a high-shear mixer operating at 2000 rpm (Dispermat F1). An ultrasonication treatment was then performed through an Hielscher UP400S sonicator for 5 min at a specific power of 460 W/cm² and a frequency of 24 kHz. The mixture was then degassed at ambient temperature and the amine hardener added and manually mixed. Finally, the mixture was degassed again at ambient temperature and poured in the cavities of a silicone mould. A curing cycle at 65 °C for 15 hr was then conducted. The same procedure was followed also for the preparation of unfilled adhesive.

The thermal properties of the samples were evaluated through differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA) tests. Experimental details are reported in [12-14]. Quasi-static tensile properties were evaluated by using an Instron 4502 electromechanical tensile testing machine, at a crosshead speed of 1 mm/min. ISO-527 1BA dogbone specimens, with a gage length of 30 mm, a width of 5 mm and a thickness of 2 mm, were tested. According to ASTM D 5045 standard, plane strain fracture toughness parameters K_{IC} and G_{IC} were evaluated on single edge notched bend (SENB) specimens (44 mm long, 10 mm wide and 4 mm thick) containing a sharp notch of about 5 mm depth. A cross-head speed of 10 mm/min was adopted in the three-point bending tests and at least five specimens were tested for each sample. fracture surfaces of SENB specimens were observed at various magnifications by a Zeiss Supra 40 field emission scanning electronic microscope (FESEM).

2.3. Preparation and characterization of single-lap bonded joints

In order to evaluate the adhesive properties of the epoxy nanocomposites, both metallic and composite single-lap joints were realized.

For adhesives filled with zirconia and alumina nanoparticles a 6082 aluminium alloy was utilized as a substrate. The procedure adopted for the joint preparation and for the control of adhesive thickness is described in [12, 13] along with specimens dimensions.

Square sheets of epoxy–glass composite laminates, having a width of 300 mm and a thickness of 2.3 mm, were prepared by hand lay up with a [0/90/-45/+45/+45/-45/90/0] lamination sequence. A bi-component epoxy resin for manual lamination, supplied by Elantas Camattini, was utilized in combination with glass fibers fabrics for the preparation of composite laminates to be utilized as adherends of the single lap joints. The procedure adopted for the joint preparation and for the control of adhesive thickness is described in [14] along with specimens dimensions.

The bonded joints were mechanically tested at ambient temperature (23 °C) under quasi-static loading conditions by using an Instron 4502 electromechanical tensile testing machine. According to ASTM D1002 standard, a crosshead speed of 1.3 mm/min was adopted. At least five specimens were tested for each sample. A nominal shear strength was computed as:

$$\tau_{\max} = \frac{F_{\max}}{A} \quad (1)$$

where F_{\max} is the maximum load registered during the tensile tests and A is the overlapping area of the joint.

Tensile fatigue tests on single-lap joints were performed by a MTS 858 Mini Bionix servohydraulic testing machine. In particular, fatigue tests were performed applying a sinusoidal stress with a frequency of 10 Hz at a load ratio of 0.1.

3 Results and discussion

3.1 Bulk adhesives

DSC tests performed on bulk adhesives evidenced how the investigated nanoparticles can markedly affect the glass transition temperature of the epoxy matrix. The obtained results are summarized in Figure 1. In the case of layered silicates a key-role is clearly played by the type of organo-modification.

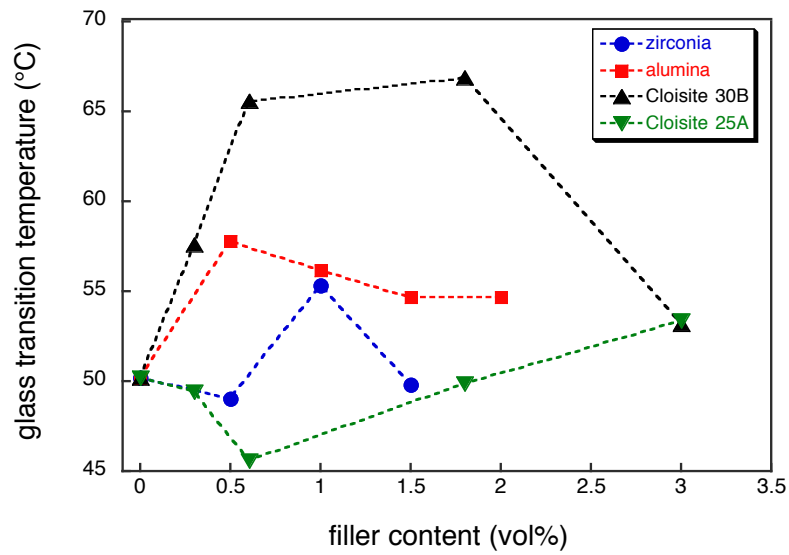


Figure 1. Glass transition temperature determined by DSC on bulk epoxy adhesives filled with various types and amounts of nanoparticles.

In order to make a more effective comparison, the fracture toughness values of bulk adhesives have been normalized on the value of the unfilled matrix, as reported in Figure 2. It clearly results that all the investigated nanofillers can effectively improve the fracture toughness of the selected epoxy adhesive. It also emerges that an optimal filler content exists at which fracture toughness is maximized.

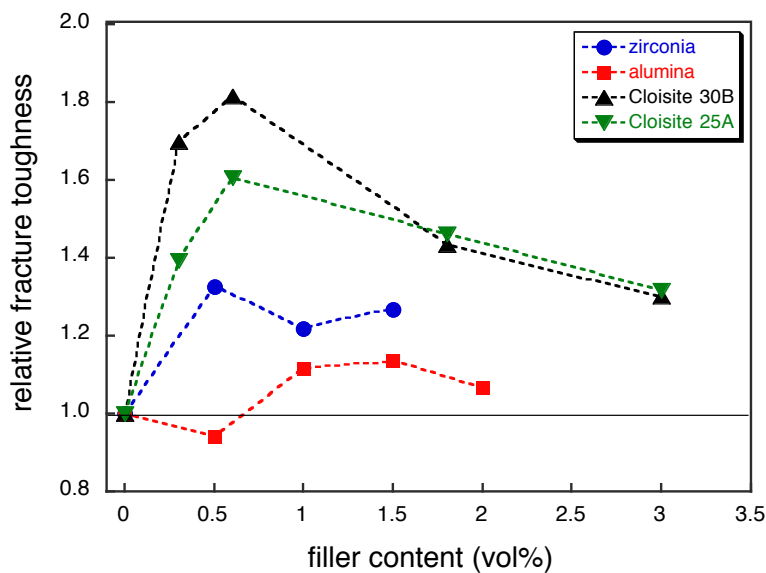


Figure 2. Relative fracture toughness of bulk epoxy adhesives filled with various types and amounts of nanoparticles.

On the basis of DSC and FESEM observations (not reported for brevity) this behaviour could be explained on the basis of the concurrent and contrasting effects of chain blocking, reduction of the crosslinking degree and filler aggregation.

3.1 Bonded joints

The load bearing capabilities of bonded joints can be remarkably improved by the nanofiller addition. In particular, the relative shear strength values reported in Figure 3 indicates that the performances of the bonded joints are influenced by the fracture toughness of bulk adhesive and by the adhesive properties with the selected substrates, with the presence of an optimal filler content.

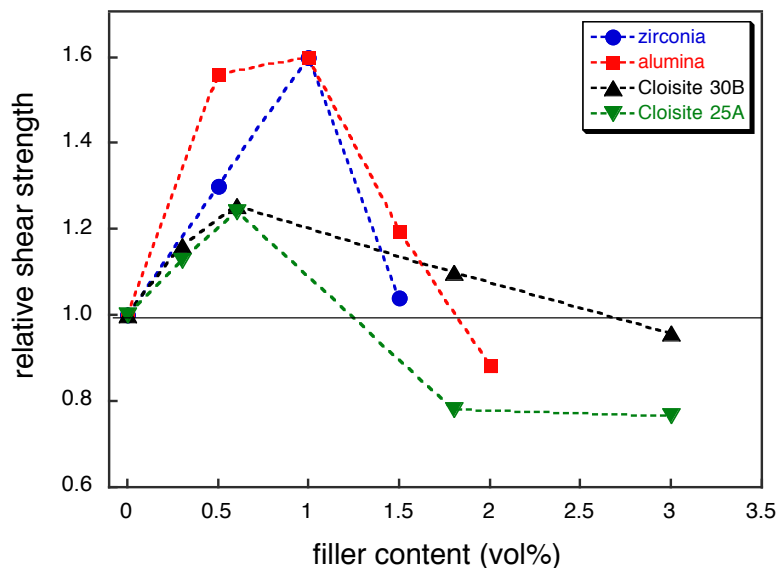


Figure 3. Relative shear strength of single-lap joints bonded with epoxy adhesives filled with various types and amounts of nanoparticles.

As reported in Figure 4, preliminary fatigue test limited to the alumina-based adhesives, indicate a beneficial effects of the nanoparticles also on the fatigue resistance of bonded joints.

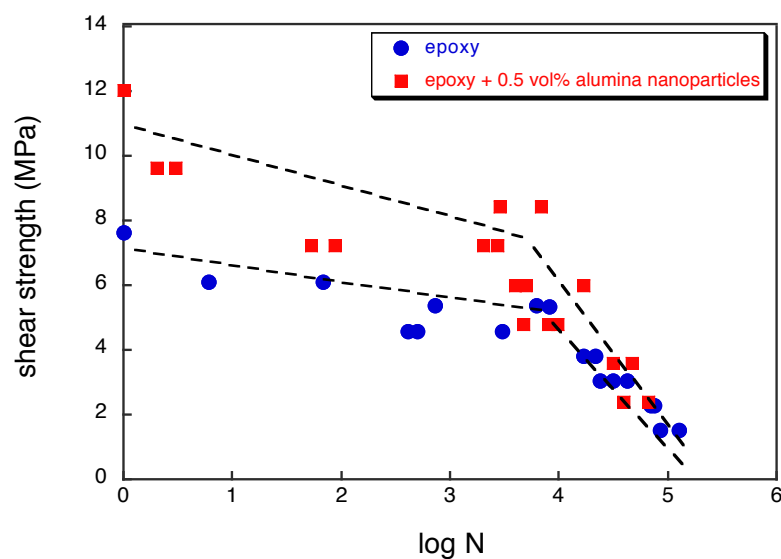


Figure 4. Fatigue S–N curves of single-lap joints bonded with pure epoxy (circle) and epoxy filled with 0.5 vol% of alumina nanoparticles.

4 Conclusions

Epoxy-based nanocomposite adhesives were prepared using various amounts of zirconia nanoparticles, alumina nanoparticles, and layered silicates. The glass transition temperature and the fracture toughness of bulk adhesives was noticeably improved by the addition of nanoparticles with a maximum value for an optimal filler concentration.

Tensile tests on single-lap joints evidenced that the introduction of nanoparticles in epoxy adhesive at filler concentrations lower than 1 vol.% led to remarkable enhancements of the static and fatigue shear resistance of the bonded joints.

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